

KOKAI PATENT APPLICATION NO. SHO 61-79644

TRANSPARENT LAMINATED CONDUCTIVE FILM

[Translated from Japanese]

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TRANSPARENT LAMINATED CONDUCTIVE FILM

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Specification

1. Title of invention

Transparent laminated conductive film

2. Claim of the invention

A layer of one or more of the oxides SiO, SiO₂, TiO₂, ZrO₂, Al₂O₃, Ta₂O₅, Nb₂O₃, SnO₂ and CeO₂ is formed on one surface of a transparent polymer film, followed by an organic material layer, and a metal oxide layer is further provided for the aforementioned organic material layer.

A transparent laminated conductive film where a film mainly comprising indium oxide is formed on one surface or both surfaces of the substrate film produced above as a conductive layer.

3. Detailed description of the invention

In the present invention, a layer of one or more oxides selected from SiO, SiO₂, TiO₂, ZrO₂, Al₂O₃, Ta₂O₅, Nb₂O₃, SnO₂ and CeO₂ is formed on one surface of a transparent polymer film,

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followed by an organic material layer, and a metal oxide layer is further formed on the aforementioned organic material layer.

And the invention pertains to a transparent laminated conductive film where a film mainly comprising indium oxide is formed as a conductive layer on one surface or both surfaces of the substrate film produced above.

For the transparent conductive material, those having a glass substrate with the surface provided with a tin oxide or indium oxide film are known and are widely used as electrodes for a variety of displays and transparent surface heating elements.

Meanwhile, in a transparent conductive film, the conventional glass substrate is replaced with a polymer film, which is lightweight, flexible, and does not crack, and furthermore, the material offers high processability and accommodates large surface areas and is a promising material for electrodes for liquid crystals.

Primarily polyester films are used in formation of transparent conductive materials, and in general, it is produced by biaxial drawing and produces birefringence, thus, use of the material for transparent electrodes of TN (Twisted Nematic) type liquid crystal display elements has not been made possible.

Thus, use of a uniaxially drawn polyester film has been studied as a transparent electrode for liquid crystal elements, but matching of the axis with optical anisotropy with the axis of the polarizing plate used for the liquid crystal element is required and productivity is very low.

Furthermore, because of uniaxial drawing, anisotropy is observed at the time of thermal shrinkage under heat and physical and optical properties of the transparent electrode are lost.

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Furthermore, cellulose type films have been studied but heat-resistance is absent and the material undergoes significant deformation during the course of fabrication; thus use of the material is not possible.

The electrode for liquid crystal display elements is not especially limited, but it is

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necessary for the material to have high transparency, to be amorphous, and to have heat resistance.

As a result of much research conducted by the present inventors on this topic, they discovered that a polymer film having birefringence within 40 degrees in terms of phase difference, photoelastic coefficient of 2.0 mm/kg or below, and thermal shrinkage factor at 200°C of 5% or below is suitable. However, it was discovered that a significant reduction in the life of the liquid crystal occurs and problems due to permeation of water vapor and air occur upon film formation, which is absent with a conventional glass substrate.

In general, scratches are likely to be produced in a polymer film and a protective coating is required from the standpoint of transparency.

Based on the above background, and as a result of many studies conducted on this topic, the present inventors discovered that permeation of water vapor and air could be prevented and life of the liquid crystal could be significantly increased when an organic material layer comprising polyvinyl alcohol with both surfaces provided with one of more transparent metal oxide layers made of materials selected from SiO, SiO₂, TiO₂, ZrO₂, Al₂O₃, Ta₂O₅, Nb₂O₃, SnO₂ and CeO₂ was formed on the base film, and that the film functioned as a protective coating for the polymer film. The invention is explained in further detail below.

First, the base film used when a laminated conductive film is used for liquid crystal is not especially limited, but it is necessary for birefringence to be absent for a phase difference of 40 degrees or more.

In general, a TN type liquid crystal display element is used under bright fields, but when the birefringence of the film is high, coloring of other areas occurs and contrast of the characters displayed is reduced.

Thus, it is desirable when birefringence in the metal oxide and organic material layer is entirely absent, but when fluctuations in the production process are taken into consideration, approximately 40 degrees of birefringence in terms of phase difference is the limit regardless of the film thickness.

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It should be noted that the aforementioned value is obtained upon measuring the phase difference based on the difference in the optical wave of the base film provided with a metal oxide layer and organic material layer in the major axis direction using a phase difference meter.

Furthermore, the photoelastic coefficient is a constant that shows likelihood of formation of birefringence when a force is applied to the film and the film undergoes deformation.

In general, in a liquid crystal cell that utilizes a film electrode, tensile or compressive stress is applied to the film electrode at the time of setting of the film electrode or bonding of the film electrode, and when high birefringence occurs in this case, the contrast of the display is reduced as described above.

An especially important point is that a liquid crystal display with a curved surface is not possible in some cases when a film electrode is used, a fair degree of tension and compression force are applied to the film, thus, in a material where high birefringence is generated under high stress, the contrast of the display is reduced for the aforementioned reasons.

Therefore, it is desirable when materials that form a lower degree of birefringence are desirable for the base film, metal oxide, and organic material layer used in the film electrode.

When a variety of transparent plastics were examined, the limit of the photoelastic coefficient was found to be 2.0 mm/kg and a value below that value is desirable.

In general, for the material having a low photoelastic coefficient, a material having a high Young's modulus, that is, a material that is less likely to distort and without molecules having high polarizability is desirable.

It should be noted that measurement of the photoelastic coefficient is done by a photoelastometer based on the relationship between the stress applied to the base film provided with an organic material layer and the photoelastic effect generated.

Furthermore, as for the thermal properties of the base film, a heat-treatment is provided at a temperature in the range of 100°C to 200°C for stabilization of the conductive layer metal oxide at the time of production of a transparent laminated conductive film, and when shrinkage of the

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film is high, stress concentration of the metal oxide film takes place resulting in wrinkles and cracks.

Furthermore, in the process used for electrode pattern formation, processes such as cleaning and drying are provided several times, and when the thermal shrinkage of the base film having a conductive metal oxide layer occurs, precision of the pattern is lost and processes that follow are affected.

And furthermore, the temperature of the device with the liquid crystal display element included becomes relatively high at times, and in the aforementioned environment, shrinkage and deformation of the electrode film take place and function is lost at times.

For the reasons given above, heat-resistance is required for the film used for the liquid crystal electrode and a shrinkage factor of 5% or below at 200°C is desirable.

In addition, when the film is used for a liquid crystal, etc., it is necessary to prevent permeation of water vapor and air.

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In each of type of liquid crystal such as schiff base, aza base, azoxy base, biphenyl base or phenyl cyclohexyl base liquid crystals that are commonly used, films are likely to be subjected to hydrolysis and permeation of water vapor has a direct effect on wear resistance.

Schiff base liquid crystal, in particular, requires special precautions.

Furthermore, when air permeation occurs, air bubbles are formed inside the liquid crystal, resulting in major problems.

Therefore, in order to replace the glass substrate with a polymer film, application to liquid crystal is not possible unless permeation of water vapor and air is prevented.

As a means to prevent the aforementioned problem, use of a base film capable of trapping water vapor and air is conceivable but in order to satisfy the aforementioned optical properties of a birefringence of 40 degrees or less and a photoelastic coefficient of 2.0 mm/kg or below, amorphous polymers are required.

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However, in general, permeability of water vapor and air of the aforementioned amorphous polymer films is high and prevention of deterioration of the liquid crystal is not possible.

As a result of much research, it was discovered that a film that surpassed the reliability test under 80°C and 90% RH and withstood 1700 hours of application could be achieved when a metal oxide layer was provided for both surfaces of an organic material layer having transmittance of at least 85% in the visible region, water vapor permeability of 3×10^{-5} g/cm²-24hr-atm or below and air permeability of 5×10^{-5} g/cm²-24hr-atm or below.

For the aforementioned metal oxide layer, at least one selected from SiO, SiO₂, TiO₂, ZrO₂, Al₂O₃, Ta₂O₅, Nb₂O₃, SnO₂ and CeO₂ is desirable and for the organic material layer used as a barrier layer, polyvinyl alcohol type resins having high intermolecular force and high functional group concentration are desirable and the aforementioned purpose can be achieved when the aforementioned organic material layer is sandwiched between layers of the aforementioned metal oxide.

The reason why the metal oxide layer and an organic material are used in combination as a barrier layer is because complete reduction of pinholes and contamination of the base film is not possible when a standard vapor-phase deposition method such as sputtering and deposition are used at the time of formation of the metal oxide onto a polymer film and single layer metal oxide cannot form an adequate barrier layer.

Meanwhile, when a single layer organic material is used as a barrier layer, and for the organic material suitable for the aforementioned purpose, cellulose type resins, polyacrylonitrile type resins, polyvinylidene chloride type resins, polyamide type resins, etc. can be mentioned and from the standpoint of high intermolecular force and high functional group concentration, polyvinyl alcohol type resins are desirable.

However, a polyvinyl alcohol type resin is a hydrophilic resin, and firm bonding with a polymer film is not possible, and furthermore, it absorbs water under high humidity and rupturing of hydrogen bonds takes place, and furthermore, density of the structure is lost and the air barrier

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property is sharply reduced.

Furthermore, polyvinyl alcohol type resin is damaged by the hydrochloric acid used as an etching solution for the conductive film; thus, use of the aforementioned resin by itself is not possible.

Therefore, in order to solve the aforementioned problem, first a polyvinyl alcohol type resin having a high air barrier property is bonded firmly to the substrate polymer film, a metal oxide having much higher air and water vapor barrier properties than the organic under coat is used so as to prevent deterioration under high humidity and furthermore, a metal oxide is provided over the polyvinyl alcohol type resin to provide hydrochloric acid resistance, all of the aforementioned problems can be eliminated.

The thickness of the aforementioned metal oxide layer is not especially limited and a thickness in the range of 100-5000 Å is desirable.

When the aforementioned thickness is 100 Å or below, formation of a continuous film is not possible, therefore, it is not possible to prevent water vapor and air permeation.

On the other hand, when the thickness exceeds 5000 Å, formation of cracks occurs.

The thickness of the organic material layer used as a barrier layer is not especially limited but from the standpoint of performance, the purpose of the present invention cannot be achieved when a barrier coating that is too thin is used, and a thickness of at least 0.5 µm is required.

On the other hand, when the aforementioned thickness exceeds 20 µm, stress becomes high and problems such as curling result.

Furthermore, prior to forming a film mainly comprising indium oxide as a conductive layer, an undercoat layer suitable for the aforementioned film may be provided on the aforementioned polymer film in order to increase scratch resistance.

As explained above, when a transparent laminated conductive film made of a polymer film base instead of conventional glass substrate is used, production of a new type of thin and flexible liquid crystal element is made possible, and furthermore, from the standpoint of production,

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handling is easy and punch fabrication is possible and productivity can be sharply increased.

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Furthermore, permeation of water vapor and air from the film side is prevented, thus, a significant increase in life is made possible and likelihood of scratching, which is a disadvantage of polymer films, can be prevented.

An example where the material is used as the electrode of a liquid crystal is described above, but a transparent laminated conductive film where the organic material layer is sandwiched between a specific metal oxide layer and a film mainly comprising indium oxide is provided for one or both surfaces of the polymer film prevents diffusion of water vapor and air from the film surface and is capable of preventing deterioration of the electrical properties and reliability for other applications as well and excellent results can be achieved.

The present invention is explained in further detail with the working examples below.
Working examples

For the base film, a polyether sulfone film with a thickness of 100 μm was used and as a metal oxide layer, SiO_2 with a thickness of 500 \AA was formed by a sputtering process, and for the organic material barrier layer, a polyvinyl alcohol resin was coated to form a thickness of 5 μm and furthermore, SiO_2 with a thickness of 500 \AA was formed by a sputtering process.

The birefringence of the aforementioned film was 20 degrees, and the photoclastic coefficient was 1.75 mm/kg, and the water vapor permeability of the aforementioned film was 3×10^{-5} g/cm²-24hr-atm, and air permeability was 5×10^{-5} g/cm²-24hr-atm, and furthermore, the transmittance in the visible light region was 87%.

On the other hand, the water vapor permeability of the base film used as a comparative example was 1×10^{-2} g/cm²-24hr-atm, and air permeability was 2×10^{-2} g/cm²-24hr-atm.

Furthermore, a transparent laminated conductive film where SiO_2 was deposited onto a base film polyether sulfone film to form a thickness of 500 \AA and a polyvinyl alcohol resin was coated to form a thickness of 5 μm , and a thin film of SiO_2 with a thickness of 500 \AA was further

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deposited and indium oxide was deposited onto the aforementioned SiO_2 by sputtering method as a conductive layer to form a thickness of 250 Å and a transparent laminated conductive film where an indium oxide was formed on the base film side of a film provided with a polyvinyl alcohol resin and SiO_2 thin film as a conductive layer were produced.

Meanwhile, as a comparative example, an indium oxide layer was directly deposited onto a base film by sputtering method to form a thickness of 250 Å to produce a transparent laminated conductive film.

Using the aforementioned three different types of transparent laminated conductive films, liquid crystal cells were produced and a reliability test was conducted under conditions consisting of a temperature of 80°C and humidity of 90% RH.

As a result, in cells comprising the former two transparent laminated conductive films of the present invention having SiO_2 thin films, polyvinyl alcohol resin, and SiO_2 thin film, application of 1700 hours, which is significantly longer than application standard, was possible. On the other hand, in the transparent laminated conductive film of a comparative example where an indium oxide thin film is provided directly on the base film, application was not possible beyond approximately 500 hours.

As explained in detail with working examples above, when a metal oxide layer and an organic layer that prevent water vapor and air permeation in a transparent laminated conductive film as in the case of the present invention, a transparent laminated conductive film with a significantly increased life of the liquid crystal can be produced.

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